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(REV. 5-93)U.S. DEPARTMENT OF COMMERCE  
PATENT AND TRADEMARK OFFICEATTORNEY'S DOCKET NUMBER  
10191/1438**TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371**

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

**09/555777**INTERNATIONAL APPLICATION NO.  
PCT/DE99/03155INTERNATIONAL FILING DATE  
(01.10.99)  
01 October 1999PRIORITY DATE(S) CLAIMED  
(02.10.98)  
02 October 1998TITLE OF INVENTION  
**METHOD FOR FABRICATING COMPOSITE MATERIALS AND REPRESENTATIVES OF SUCH COMPOSITE MATERIALS**

APPLICANT(S) FOR DO/EO/US

**KNOLL, Guenter; LINDEMANN, Gert; LINDNER, Friederike; WIEDMAIER, Matthias**

Applicant(s) herewith submit to the United States Designated/Elected Office (DO/EO/US) the following items and other information

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) immediately rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☐ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
  - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☒ has been transmitted by the International Bureau
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US)
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
  - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☐ have been transmitted by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☒ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)) (unsigned).
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern other document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.  
☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☒ Other items or information: International Search Report and Form PCT/RO/101.

Express Mail No.

**EM 360466549US.**

U.S. APPLICATION NO. if known, see  
37 C.F.R. 1.5

09/555777

INTERNATIONAL APPLICATION NO.

PCT/DE99/03155

ATTORNEY'S DOCKET NUMBER

10191/1438

17. ☒ The following fees are submitted:**Basic National Fee (37 CFR 1.492(a)(1)-(5)):**

Search Report has been prepared by the EPO or JPO ..... \$840.00

International preliminary examination fee paid to USPTO (37 CFR 1.482) .... \$670.00

No international preliminary examination fee paid to USPTO (37 CFR 1.482) but  
international search fee paid to USPTO (37 CFR 1.445(a)(2)) ..... \$690.00Neither international preliminary examination fee (37 CFR 1.482) nor international  
search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... \$970.00International preliminary examination fee paid to USPTO (37 CFR 1.482) and all  
claims satisfied provisions of PCT Article 33(2)-(4) ..... \$96.00

CALCULATIONS | PTO USE ONLY

**ENTER APPROPRIATE BASIC FEE AMOUNT =** \$ 840Surcharge of \$130.00 for furnishing the oath or declaration later than ☐ 20 ☐ 30 months  
from the earliest claimed priority date (37 CFR 1.492(e)).

\$

Claims

Number Filed

Number Extra

Rate

Total Claims

27 - 20 =

7

X \$18.00

\$ 126

Independent Claims

2 - 3 =

0

X \$78.00

\$ 0

Multiple dependent claim(s) (if applicable)

+ \$260.00

\$ 0

**TOTAL OF ABOVE CALCULATIONS =** \$ 966Reduction by 1/2 for filing by small entity, if applicable. Verified Small Entity statement must  
also be filed. (Note 37 CFR 1.9, 1.27, 1.28).

\$

**SUBTOTAL =** \$ 966Processing fee of \$130.00 for furnishing the English translation later than ☐ 20 ☐ 30  
months from the earliest claimed priority date (37 CFR 1.492(f)).

+

\$

**TOTAL NATIONAL FEE =** \$ 966Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be  
accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property

+

\$

**TOTAL FEES ENCLOSED =** \$ 966Amount to be:  
refunded

\$

charged

\$

a. ☐ A check in the amount of \$\_\_\_\_\_ to cover the above fees is enclosed.b. ☒ Please charge my Deposit Account No. 11-0600 in the amount of \$966.00 to cover the above fees. A duplicate copy of this  
sheet is enclosed.c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit  
Account No. 11-0600. A duplicate copy of this sheet is enclosed.**NOTE:** Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must  
be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

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SIGNATURE

Richard L. Mayer, Reg. No. 22,490  
NAME

DATE

6/2/00

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicant(s) : Guenter KNOLL et al.  
Serial No. : To Be Assigned  
Filed : Herewith  
For : METHOD FOR FABRICATING COMPOSITE  
MATERIALS AND REPRESENTATIVES  
OF SUCH COMPOSITE MATERIALS  
Art Unit : To Be Assigned  
Examiner : To Be Assigned

Assistant Commissioner  
for Patents  
Washington, D.C. 20231

**PRELIMINARY AMENDMENT**

SIR:

Please amend the above-identified application before examination, as set forth below.

**IN THE SPECIFICATION:**

Page 1, delete line 1.

Page 1, before line 3, insert:

--FIELD OF THE INVENTION--.

Page 1, before line 8, insert:

--BACKGROUND INFORMATION--.

Page 1, line 8, change "Composite" to --There are composite--.

Page 1, line 9, delete "are generally known".

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Page 1, delete lines 10 to 12, and insert --hot pressing (unconfined sintering under pressure) is discussed in German Published Patent Application Nos. 37 34 274 and 36 06 403, in which the parent substance contains  $\text{Si}_3\text{N}_4$  and the metal silicide  $\text{MoSi}_2$ , and in European Patent Application No. 0 335 382, in which the parent substance contains  $\text{Si}_3\text{N}_4$  and  $\text{MO}_5\text{Si}_3$  as the metal silicide--.

Page 1, line 13, change "containing" to --contains--.

Page 1, line 15, change "The" to --It is believed that the--.

Page 1, line 16, change ". The" to --, and that the--.

Page 1, delete line 20, and insert --German Published Patent Application No. 195 00 832, i.e., European Patent Application No. 0 721 925, discusses the--.

Page 1, line 24, change "are preferably" to --may be--.

Page 2, delete line 3.

Page 2, before line 5, insert:

--SUMMARY OF THE INVENTION--.

Page 2, line 5, change "The object of" to --An object of an exemplary embodiment of--.

Page 2, delete line 11, and insert --In an exemplary method, where  $\text{Me}_5\text{Si}_3$  is--.

Page 2, line 18, change "The inventors discovered a way to" to --To--.

Page 2, line 20, change "properties. They" to --properties, it was--.

Page 2, line 22, change "they found" to --it was found that there is--.

Page 2, delete line 24, and insert --finished composite material. In this manner, composite materials were fabricated--.

Page 2, line 27, change "method" to --exemplary method--.

Page 2, line 29, change "exhibit" to --are believed to--.

Page 2, line 31, change "It is not critical when the" to --The--.

Page 3, delete lines 3 to 18, and insert:

--BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows in a diagram, with respect to a sintering temperature, the logarithm of the lower and upper limit values of the  $N_2$  partial pressures, applicable in the method of the exemplary embodiment according to the present invention, for fabricating a composite material containing  $Mo_5Si_3$ .

Figure 2 shows in another diagram, with respect to the sintering temperature, the logarithm of the lower and upper limit values of the  $N_2$  partial pressures, applicable in the method of the exemplary embodiment according to the present invention, for fabricating a composite material containing  $Nb_5Si_3$ --.

Page 3, before line 20, insert:

--DETAILED DESCRIPTION--.

Page 3, line 21, change ", in fact," to --believed to be--.

Page 3, line 22, change "may" to --suitably appropriate--.

Page 3, line 25, change "- in" to --(in--.

Page 3, line 26, change "- preferably -" to --, which may be done--.

Page 4, line 4, change "preferably" to --which may occur, for example,--.

Page 4, line 5, change "and preferably" to --including--.

Page 5, line 1, change "with the" to --with the exemplary embodiment of the method of the--.

Page 5, line 13, change "is preferably" to --may be--.

Page 5, lines 14 and 15, change "quite preferably" to --including--.

Page 5, line 19, change "system" to --table or system--.

Page 5, line 22, change "method" to --exemplary embodiment of the method--.

Page 6, line 11, change "Besides" to --Besides the fact--.

**IN THE ABSTRACT:**

Delete lines 1 to 14, and insert:

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**ABSTRACT OF THE DISCLOSURE**

A method for manufacturing composite materials from a parent substance containing silicon nitride and metal silicide, having fixed electrical properties. The molded articles are made, virtually with their final contours, prior to a sintering operation. The parent substance containing  $\text{Si}_3\text{N}_4$  and a metal silicide is subjected to a gas pressure sintering in a nitrogenous atmosphere. The metal silicide is of the form  $\text{Me}_5\text{Si}_3$ , where Me is a metal. As a function of a sintering temperature, a lower limit of partial nitrogen pressures is selected so that  $\text{Si}_3\text{N}_4$  is stable at the lower limit and an upper limit of the partial nitrogen pressures is selected so that  $\text{Me}_5\text{Si}_3$  is stable at the upper limit. The resulting composite material is a silicon-containing composite material made of  $\text{Si}_3\text{N}_4$  and the metal silicide. The metal silicide is selected from the group of  $\text{Nb}_5\text{Si}_3$ ,  $\text{V}_5\text{Si}_3$ ,  $\text{Ta}_5\text{Si}_3$  and  $\text{W}_5\text{Si}_3$ .

**IN THE CLAIMS:**

On the first page of the claims, first line, change "Patent Claims" to:

--WHAT IS CLAIMED IS:--.

Please cancel original claims 1 to 27, without prejudice, and please add new claims 28 to 54 as follows:

--28. (New) A method for fabricating a composite material, the method comprising the steps of:

providing a parent substance containing a silicon nitride and a metal silicide, the silicon nitride being  $\text{Si}_3\text{N}_4$  and the metal silicide being of a form  $\text{Me}_5\text{Si}_3$ , where Me is a metal;

establishing, as a function of a sintering temperature, an upper limit and a lower limit of partial nitrogen pressures so that the silicon nitride is stable at the lower limit and the metal silicide is stable at the upper limit; and

gas pressure sintering the parent substance in a nitrogenous atmosphere based on the lower limit and the upper limit.

29. (New) The method of claim 28, wherein the metal of the metal silicide is selected from a metal of one of a 5th subgroup and a 6th subgroup of the periodic table.

30. (New) The method of claim 29, wherein the metal of the metal silicide is selected from the group of Mo, Nb, V, Nb, Ta and W.

31. (New) The method of claim 28, wherein a weight ratio of  $\text{Si}_3\text{N}_4:\text{Me}_5\text{Si}_3$  is between about 20:80 and about 80:20.

32. (New) The method of claim 28, wherein the parent substance includes sinter additives.

33. (New) The method of claim 32, wherein the sinter additives include at least one of aluminum oxide and yttrium oxide.

34. (New) The method of claim 32, wherein a concentration of the sinter additives in an initial mixture is retained at less than about 10 % by weight.

35. (New) The method of claim 28, wherein the parent substance includes pressing agents and binding agents.

36. (New) The method of claim 28, wherein the parent substance is ground into a powder.

37. (New) The method of claim 28, further comprising one of the following sets of steps:

(a) forming the parent substance into a desired shape by one of ceramic injection molding and cold-isostatic pressing before the step of gas pressure sintering; and

(b) (i) forming the parent substance into the desired shape by the one of the ceramic injection molding and the cold-isostatic pressing before the step of gas pressure sintering, and

(ii) forming the composite material by green processing subsequent to the step of gas pressure sintering.

38. (New) The method of claim 28, wherein the parent substance is cold-isostatically compressed at a pressure of between about 100 MPa and about 300 MPa.

39. (New) The method of claim 28, further comprising the step of pre-sintering the parent substance prior to the step of gas pressure sintering.

40. (New) The method of claim 39, wherein the step of pre-sintering is performed at a temperature of between about 500°C and about 700°C.

41. (New) The method of claim 39, wherein the step of pre-sintering is performed at a pressure of between about 0.05 MPa and about 0.2 MPa.

42. (New) The method of claim 28, wherein the step of gas pressure sintering is performed at a temperature of between about 1700°C and about 1900°C.



43. (New) The method of claim 28, wherein the step of gas pressure sintering is performed at a partial N<sub>2</sub> pressure of between about 0.5 MPa and about 1.0 MPa.

44. (New) The method of claim 29, wherein:

the metal of the metal silicide is molybdenum; and

the upper limit is set as an upper limit of partial N<sub>2</sub> pressures (p<sub>N2</sub>)

according to a first equation of  $y_1 = 5.3071 \cdot \ln(T) - 37.014$ , and

the lower limit is set as a lower limit of the partial N<sub>2</sub> pressures (p<sub>N2</sub>)

according to a second equation of  $y_2 = 7.3494 \cdot \ln(T) - 54.124$ ,

where  $y_1$  and  $y_2$  represent  $\lg(p_{N2} [\text{bar}])$  values.

45. (New) The method of claim 29, wherein:

the metal of the metal silicide is niobium; and

the upper limit is set as an upper limit of partial N<sub>2</sub> pressures (p<sub>N2</sub>)

according to a first equation of  $y_1 = 7.8968 \cdot \ln(T) - 58.8$ , and

the lower limit is set as a lower limit of the partial N<sub>2</sub> pressures (p<sub>N2</sub>)

according to a second equation of  $y_2 = 8.2598 \cdot \ln(T) - 62.064$ ,

where  $y_1$  and  $y_2$  represent  $\lg(p_{N2} [\text{bar}])$  values.

46. (New) The method of claim 28, wherein the step of gas pressure sintering is performed in a gas-pressure sintering furnace.

47. (New) A silicon-containing composite material comprising a silicon-containing material made of Si<sub>3</sub>N<sub>4</sub> and a metal silicide, wherein the metal silicide is selected from the group of Nb<sub>5</sub>Si<sub>3</sub>, V<sub>5</sub>Si<sub>3</sub>, Ta<sub>5</sub>Si<sub>3</sub> and W<sub>5</sub>Si<sub>3</sub>.

48. (New) The composite material of claim 47, wherein the metal silicide contains carbon.

49. (New) The composite material of claim 48, wherein the metal silicide contains carbon with a concentration specific to the composite material of about 0.3 % by weight to about 0.6 % by weight.

50. (New) The composite material of claim 47, wherein a mass ratio of  $\text{Si}_3\text{N}_4:\text{Me}_5\text{Si}_3$  is between about 20:80 and about 80:20.

51. (New) The composite material of claim 47, wherein the parent substance includes sinter additives.

52. (New) The composite material of claim 51, wherein the sinter additives include at least one of aluminum oxide and yttrium oxide.

53. (New) The composite material of claim 51, wherein a concentration of the sinter additives in an initial mixture is less than about 10 % by weight.

54. (New) The composite material of claim 47, wherein the metal silicide is  $\text{Nb}_5\text{Si}_3$ .

#### **Remarks**

This Preliminary Amendment cancels, without prejudice, original claims 1 to 27 in the underlying PCT Application No. PCT/DE99/03155, and adds new claims 28 to 54. The new claims conform the claims to U.S. Patent and Trademark Office rules and do not add new matter to the application.

The above amendments to the specification and abstract are to conform the specification and abstract to U.S. Patent and Trademark Office rules or to correct informalities, and do not introduce new matter into the application.

The underlying PCT Application No. PCT/DE99/03155 includes an International Search Report, dated March 8, 2000. The Search Report includes a list of documents that were uncovered in the underlying PCT Application. A copy of the Search Report accompanies this Preliminary Amendment.

Applicants assert that the subject matter of the present application is new, non-obvious, and useful. Prompt consideration and allowance of the application are respectfully requested.

Respectfully Submitted,

KENYON & KENYON

Dated: 6/2/00

By: *Richard L. Mayer*  
Richard L. Mayer  
Reg. No. 22,490

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# METHOD FOR FABRICATING COMPOSITE MATERIALS AND REPRESENTATIVES OF SUCH COMPOSITE MATERIALS

## Background of the Invention

The present invention relates to a method for fabricating a composite material out of a parent substance containing silicon nitride and a metal silicide, through gas pressure sintering in a nitrogenous atmosphere and a silicon-containing composite material, whose silicon-containing constituents are made of  $\text{Si}_3\text{N}_4$  and of a metal silicide.

Composite materials, which contain silicon nitride and metal silicide, and methods for their preparation are generally known. The fabrication of such materials through single-axial hot-pressing (unconfined sintering under pressure) is described in German patents DE 37 34 274 C2 and DE 36 06 403 C2, the parent substance containing  $\text{Si}_3\text{N}_4$  and, as silicide,  $\text{MoSi}_2$ , and in the EP 0 335 382 A1, the parent substance containing  $\text{Si}_3\text{N}_4$ ,  $\text{Mo}_5\text{Si}_3$  as silicide and carbon, and the fabricated material containing as metal silicide,  $\text{Mo}_5\text{Si}_3\text{C}$  or, more precisely,  $\text{Mo}_{5-X}\text{Si}_3\text{C}_{1-Y}$  ( $0 \leq X \leq 2$ ;  $0 \leq Y \leq 1$ ). The electrical properties of the materials fabricated in this manner are able to be selectively adjusted. The method is industrial and requires considerable outlay for energy consumption. The application of the method only permits fabrication of complex geometrical structures in expensive, hard-machining operations.

German Patent DE 195 00 832 A1, i.e., European Patent EP 0 721 925 A2 discuss the fabrication of highly heat-resistant silicon nitride composite materials, which contain a reinforcement component of  $\text{Me}_5\text{Si}_3$  and, moreover,  $\text{MeSi}_2$  or  $\text{MeSi}_3$ , and silicides of other stoichiometries, Me standing for metal. Mixed into the parent substance as metal silicide are  $\text{MeSi}_2$  and  $\text{Me}_5\text{Si}_3$ , or only  $\text{MeSi}_2$ . The metals are preferably selected from the group including molybdenum, tungsten, chromium, tantalum, niobium, manganese and vanadium. The sintering is performed as gas pressure sintering (at  $\text{N}_2$  pressures of 100 bar), which makes it possible to fabricate molded articles (shaped bodies), virtually with their final contours, in ceramic injection molding or pressing processes, with subsequent green processing, or in hot-pressing (sintering under pressure) processes. Special electrical properties cannot be

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adjusted.

## The Present Invention and Advantages Thereof

5 The object of the present invention is an industrially simple and energy-saving method for fabricating composite materials containing silicon nitride and metal silicide and having fixed electrical properties, which makes it possible to manufacture the molded articles, virtually with their final contours, from the composite material, prior to the sintering operation, and to specify representatives of such composite materials.

10 This objective is achieved by a method of the type mentioned at the outset, where  $\text{Me}_5\text{Si}_3$  is introduced as the metal silicide into the parent substance, the partial pressure of the nitrogen being established as a function of the sintering temperature in such a way that, at the lower limit of the practical range,  $\text{Si}_3\text{N}_4$  is still thermodynamically stable and, at the upper limit,  $\text{Me}_5\text{Si}_3$ , and is dissolved into a composite material of the type mentioned at the outset, the metal silicide being selected from the group  $\text{Nb}_5\text{Si}_3$ ,  $\text{V}_5\text{Si}_3$ ,  $\text{Ta}_5\text{Si}_3$  and  $\text{W}_5\text{Si}_3$ .

15 The inventors discovered a way to exploit the advantages of the gas-pressure sintering method, at the same time while manufacturing composite materials having fixed electrical properties. They ascertained that the electrical properties cannot be adjusted in a determinate fashion (definably) when  $\text{N}_2$  partial pressures are applied above a specific pressure range.

20 During test trials, they found a range of the  $\text{N}_2$  partial pressures within which one can prevent other silicon-containing components, besides  $\text{Si}_3\text{N}_4$  and  $\text{Me}_5\text{Si}_3$ , from being present in the finished composite material. In this manner, they were able to fabricate composite materials having fixed electrical properties. In comparison to the hot-pressing (sintering under pressure) method, the gas-pressure sintering method makes do with a much simpler sintering device. Compact, high-strength materials are able to be fabricated with the method according to the present invention. In comparison to materials containing  $\text{MeSi}_2$ , materials containing  $\text{Me}_5\text{Si}_3$  exhibit a very low temperature dependency of the electrical conductivity.

25 It is not critical when the method is carried out in such a way that the metal silicide in the composite material has a carbon concentration (preferably between about 0.3 and about 0.6 %

by weight specific to the composite material), i.e., is present as  $\text{Me}_5\text{Si}_3(\text{C})$ .

Further advantageous refinements of the method according to the present invention and of the composite materials according to the present invention are delineated in the dependent claims.

#### Drawing

In the following, the present invention is elucidated on the basis of exemplary embodiments illustrated in the drawing, whose figures show:

Figure 1 plotted in a diagram over the sintering temperature, the logarithm of the lower and upper limit values of the  $\text{N}_2$  partial pressures, applicable in the method according to the present invention, for fabricating a composite material containing  $\text{Mo}_5\text{Si}_3$ ; and

Figure 2 the same as in Figure 1, however, for fabricating a composite material containing  $\text{Nb}_5\text{Si}_3$ .

The exemplary embodiments of the method according the present invention described in the following are, in fact, particularly advantageous. However, they are merely provided by way of example, and many variations are possible, without departing from the scope of the claims.

To fabricate the composite materials, a preconditioned  $\text{Si}_3\text{N}_4$  powder is first mixed with sinter additives, such as  $\text{Al}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$ , or the like, which - in terms of the entire inorganic concentration -, make up less than about 10% by weight,  $\text{Me}_5\text{Si}_3$  in suitable percentages by weight and, in some instances, organic pressing and/or binding agents, with the addition of an organic solvent - preferably - in an attritor mill. The attrited suspension is dried, for example, in a rotary evaporator. From the dried powder, through cold-isostatic pressing at pressures of between about 150 and 250 MPa, molded articles are produced, which, subsequent to the pressing operation, can obtain their final shape in a green processing. Other processing possibilities following the introduction of appropriate binding agents, include ceramic

injection molding (CIM) or extrusion. For debinding and/or presintering purposes, the molded articles are treated at approximately 600°C under a pressure of 1 bar in an inert gas atmosphere for about two hours, the organic constituents being removed, virtually without leaving any residues. The main sintering operation then follows, preferably in a gas-pressure sintering furnace at a temperature within a range of about 1700 and 1900°C, and preferably between about 1800 and 1900°C, under a defined partial N<sub>2</sub> pressure (total pressure between about 0.1 MPa and 10 MPa), which is set so as to achieve thermodynamic equilibrium of the Si<sub>3</sub>N<sub>4</sub> phase and the Me<sub>5</sub>Si<sub>3</sub> or Me<sub>5</sub>Si<sub>3</sub>(C) phase during the sintering compression, i.e., to ensure they do not enter into any chemical reactions. The usable range of the partial N<sub>2</sub> pressure at a specific temperature is dependent upon the metal silicide. In the diagrams of Figures 1 and 2, the ranges of the usable partial N<sub>2</sub> pressures, measured in bar, (p<sub>N2</sub>) for mixtures containing Mo<sub>5</sub>Si<sub>3</sub> or Nb<sub>5</sub>Si<sub>3</sub> are plotted as log(p<sub>N2</sub> [bar]) as a function of the temperature. In each case, the upper and lower limiting curves satisfy, for Mo-containing mixtures, the equations

$$y_1 = 5.3071 \cdot \ln(T) - 37.014$$

respectively

$$y_2 = 7.3494 \cdot \ln(T) - 54.124$$

and, for Nb-containing mixtures, the equations

$$y_1 = 7.8968 \cdot \ln(T) - 58.8$$

respectively

$$y_2 = 8.2598 \cdot \ln(T) - 62.064,$$

y<sub>1</sub> and y<sub>2</sub> representing lg(p<sub>N2</sub> [bar]) values. Below the limited range, Si<sub>3</sub>N<sub>4</sub> reacts with Me<sub>5</sub>Si<sub>3</sub>.

Above the limited range, Me<sub>5</sub>Si<sub>3</sub> reacts with nitrogen. The curves were determined in serial investigations, in that, at a fixed temperature of between about 1700 and 1900°C, the partial N<sub>2</sub> pressures were determined at which Me<sub>5</sub>Si<sub>3</sub> and Si<sub>3</sub>N<sub>4</sub> are thermodynamically stable. The criterion that no reaction took place is, in each case, that only the desired silicon-containing phases are found in the X-ray diffractogram of the sintered material. The equations named above were then determined on the basis of these values, of known data, such as enthalpies of formation, and of thermodynamic functions. The sintering process takes about two to five hours.

The specific electrical resistance of the composite materials fabricated in accordance with the present invention is adjusted through the selection of the metal in the silicide and the concentration and the distribution of the silicide in the composite material. Beyond the particular percolation range, specific electrical resistances of between about  $1.7 \cdot 10^{-4} \Omega \text{cm}$  and  $1 \cdot 10^{12} \Omega \text{cm}$  can be reproducibly adjusted with materials containing  $\text{Nb}_5\text{Si}_3(\text{C})$ , and of between about  $1 \cdot 10^{-5} \Omega \text{cm}$  and  $1 \cdot 10^{12} \Omega \text{cm}$  with materials containing  $\text{Mo}_5\text{Si}_3(\text{C})$ . The specific resistance is measured using the four-point method.

Using qualitative and quantitative chemical and physico-chemical analyses and radiographic phase analysis, one can verify that - apart from the carbon concentration and without consideration of the organic constituents - the sintered materials have the same composition as the mixture that the fabrication process originated with. During the sintering process in a graphite furnace, the carbon is preferably contained in the metal silicide with a concentration, in terms of the composite material, of between about 0.3 and 0.6 % by weight, and quite preferably with about 0.5 % by weight. The room (ambient) temperature stabilities of the composite materials do not lie under 500 MPa.

Besides standing for niobium and molybdenum having comparable results for all metals of the 5th and 6th subgroup of the periodic system, Me can stand, in particular, for vanadium, tantalum, chromium and tungsten.

The method of the present invention is described in greater detail in the following on the basis of two special examples.

#### Example 1

The parent substance was mixed from 36 % by weight of  $\text{Si}_3\text{N}_4$ , 1.7 % by weight of  $\text{Al}_2\text{O}_3$ , 2.38 % by weight of  $\text{Y}_2\text{O}_3$ , 60  $\text{Nb}_5\text{Si}_3$  % by weight and the usual pressing and/or binding agents. The average particle size of the  $\text{Si}_3\text{N}_4$  was  $0.7 \mu\text{m}$ , and that of the  $\text{Nb}_5\text{Si}_3$   $0.7 \mu\text{m}$ . The cold isostatic compression at 200 MPa was followed by a pre-sintering under an inert gas at up to  $600^\circ\text{C}$ , argon being used (nitrogen also could have been used). Sintering subsequently took place at a partial  $\text{N}_2$  pressure of 0.5 MPa (total pressure 1 MPa) and  $1800^\circ\text{C}$  in a



graphite furnace.

The density of the composite material obtained was 97% of the material density. The radiographic phase analysis performed after the sintering process yielded exclusively  $\text{Si}_3\text{N}_4$  and  $\text{Nb}_5\text{Si}_3(\text{C})$  as silicon-containing phases. As a specific electrical resistance,  $3 \cdot 6 \cdot 10^{-3} \Omega \text{cm}$  was determined at  $25^\circ \text{C}$ . The temperature coefficient of the specific electrical resistance amounted to  $2 \cdot 10^{-4} \text{ K}^{-1}$ .

#### Example 2

Besides that the inorganic constituents of the parent substance were made up of 54 % by weight of  $\text{Si}_3\text{N}_4$ , 2.6 % by weight of  $\text{Al}_2\text{O}_3$ , 3.4 % by weight of  $\text{Y}_2\text{O}_3$ , 40  $\text{Nb}_5\text{Si}_3$  % by weight, the method was carried out in the same manner as in Example 1.

The analyses performed on the sintered material likewise yielded the attained material density amount of 97%, the radiographic phase analysis yielded exclusively  $\text{Si}_3\text{N}_4$  and  $\text{Nb}_5\text{Si}_3(\text{C})$  as silicon-containing phases, and  $2 \cdot 10^2 \Omega \text{cm}$  at  $25^\circ \text{C}$  was determined as a specific electrical resistance.

## Patent Claims

1. A method for fabricating a composite material out of a parent substance containing silicon nitride and metal silicide, through gas pressure sintering in a nitrogenous atmosphere, characterized in that, as metal silicide,  $\text{Me}_5\text{Si}_3$  is introduced into the parent substance, the partial nitrogen pressure is established as a function of the sintering temperature in such a way that, still stable at the lower limit of the practical range is  $\text{Si}_3\text{N}_4$  and, at the upper limit,  $\text{Me}_5\text{Si}_3$ .
2. The method as recited in Claim 1, characterized in that the metal in the silicide is selected from a metal of the 5th or 6th subgroup.
3. The method as recited in Claim 2, characterized in that the metal is selected from the group Mo, Nb, V, Nb, Ta and W.
4. The method as recited in one of Claims 1 through 3, characterized in that a weight ratio of between about 20:80 and 80:20 is adjusted for  $\text{Si}_3\text{N}_4$ : $\text{Me}_5\text{Si}_3$ .
5. The method as recited in one of Claims 1 through 4, characterized in that sinter additives are added to the parent substance.
6. The method as recited in Claim 5, characterized in that aluminum oxide and/or yttrium oxide and/or similarly acting materials are added as sinter additives.
7. The method as recited in Claim 5 or 6, characterized in that the concentration of sinter additives in the initial mixture is retained at < about 10 % by weight.
8. The method as recited in one of Claims 1 through 7, characterized in that pressing and/or binding agents are added to the parent substance.
9. The method as recited in one of Claims 1 through 8, characterized in that the parent substance is ground.



representing  $\lg(p_{N_2} [\text{bar}])$  values.

19. The method as recited in one of the Claims 1 through 18, characterized in that the sintering is carried out in a gas-pressure sintering furnace.

20. A silicon-containing composite material, whose silicon-containing constituents are made of  $\text{Si}_3\text{N}_4$  and of a metal silicide, characterized in that the metal silicide is selected from the group  $\text{Nb}_5\text{Si}_3$ ,  $\text{V}_5\text{Si}_3$ ,  $\text{Ta}_5\text{Si}_3$  and  $\text{W}_5\text{Si}_3$ .

21. The composite material as recited in Claim 20, characterized in that the metal silicide contains carbon.

22. The composite material as recited in Claim 21, characterized in that the metal silicide contains carbon with a concentration specific to the composite material of about 0.3 to about 0.6 % by weight.

23. The composite material as recited in one of Claims 20 through 22, characterized in that the mass ratio of  $\text{Si}_3\text{N}_4:\text{Me}_5\text{Si}_3$  is between about 20:80 and 80:20.

24. The composite material as recited in one of Claims 20 through 23, characterized in that sinter additives are added to the parent substance.

25. The composite material as recited in Claim 24, characterized in that the sinter additives are made of aluminum oxide and/or yttrium oxide and/or similarly acting materials.

26. The composite material as recited in Claim 24 or 25, characterized in that the concentration of sinter additives in the initial mixture is < about 10 % by weight.

27. The composite material as recited in one of Claims 20 through 26, characterized in that the metal silicide is  $\text{Nb}_5\text{Si}_3$ .

## Abstract

To manufacture composite materials containing silicon nitride and metal silicide and having fixed electrical properties, in an industrially simple and energy-saving fashion, the aim being to produce the molded articles, virtually with their final contours, from the composite materials, prior to the sintering operation, and to specify representatives of such composite materials, a method is proposed where a parent substance containing  $\text{Si}_3\text{N}_4$  and metal silicide is subjected to the gas pressure sintering in a nitrogenous atmosphere, where, as metal silicide,  $\text{Me}_5\text{Si}_3$  is introduced into the parent substance, where the partial nitrogen pressure is established as a function of the sintering temperature in such a way that, still stable at the lower limit of the practical range is  $\text{Si}_3\text{N}_4$  and, at the upper limit,  $\text{Me}_5\text{Si}_3$  and a silicon-containing composite material, whose silicon-containing constituent is made of  $\text{Si}_3\text{N}_4$  and of a metal silicide, the metal silicide being selected from the group  $\text{Nb}_5\text{Si}_3$ ,  $\text{V}_5\text{Si}_3$ ,  $\text{Ta}_5\text{Si}_3$  and  $\text{W}_5\text{Si}_3$ .

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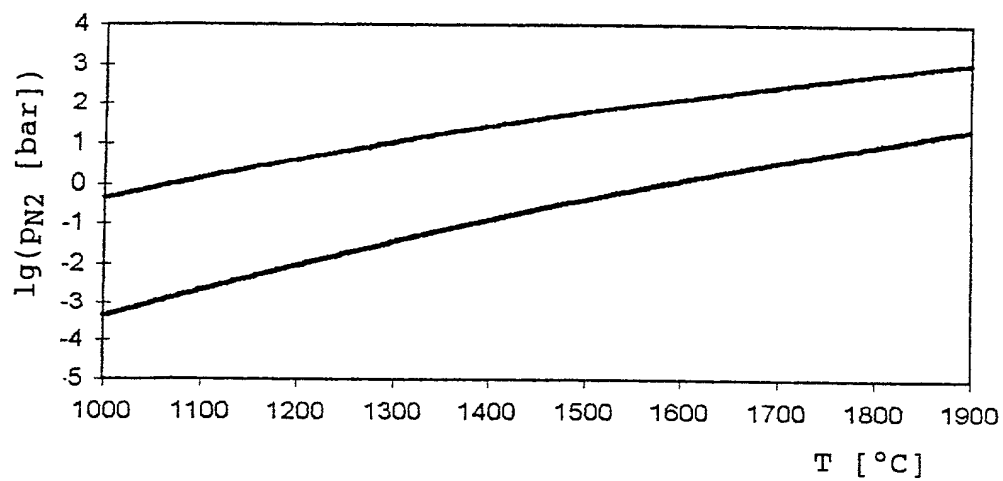


Fig. 1

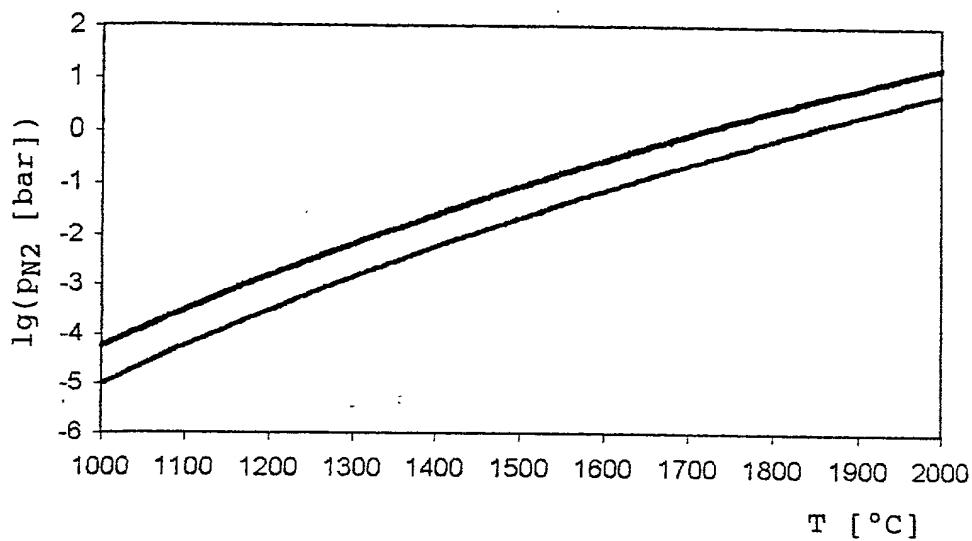


Fig. 2

DECLARATION AND POWER OF ATTORNEY

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled **METHOD FOR FABRICATING COMPOSITE MATERIALS AND REPRESENTATIVES OF SUCH COMPOSITE MATERIALS**, the specification of which was filed as PCT International Application No. **PCT/DE99/03155** on October 1, 1999 and as U.S. Application Serial No. 09/555,777.

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, § 1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, § 119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application(s) for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

PRIOR FOREIGN APPLICATION(S)

Number	Country filed	Day/month/year	Priority Claimed Under 35 USC 119
198 45 532.1	Fed. Rep. of Germany	2 October 1998	Yes

2 And I hereby appoint Richard L. Mayer (Reg. No. 22,490) and Gerard A. Messina (Reg. No. 35,952) my attorneys with full power of substitution and revocation, to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith.

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful and false statements may jeopardize the validity of the application or any patent issued thereon.





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